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Subject: SCOPING STUDIES TO IDENTIFY FORMS OF MERCURY IN ACID PIT
SOIL SAMPLES - GSG-10-97

The attached report is provided for your perusal.

GSG

Attachment

cc: K. J. Holdren, MS 2107
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Scoping Studies to Identify Forms of Mercury in Acid Pit Soil Samples

INTRODUCTION

The identification of the chemical species of mercury (Hg) is important because it has a large bearing on the mobility of the metal in the environment (Francis 1985; Evans 1989). Mercury identification is particularly significant at the Radioactive Waste Management Complex (RWMC) acid pit in which Hg was buried as nitric acid solutions that originated from fuel rod dissolution processes. Information on the chemical forms of the Hg compounds beneath the acid pit is needed to establish the species partition coefficients (K_d), which then will permit defensible risk evaluation calculations.

A large body of work has been done to establish methods for the identification of organic Hg species (Bloom 1991). However, no viable approaches have been developed for the identification of inorganic Hg species on mineral surfaces. Research to use secondary ion mass spectrometry (SIMS) for the characterization of inorganic Hg species is described below.

APPROACH

A characterization strategy for Hg species that is primarily nondestructive is needed to preserve the molecular information. This constraint eliminates many standard Hg detection analysis strategies that rely on the dissolution of the Hg-containing sample before the detection of atomic Hg. A class of analysis that is inherently nondestructive is surface analysis. However, this class historically has suffered from a lack of sensitivity.

A type of surface analysis that may have high sensitivity is SIMS, which is an area of research emphasis at the Idaho National Engineering and Environmental Laboratory. The approach to the characterization of Hg species described herein is to use novel SIMS instrumentation for the investigation of Hg salts, red clay samples exposed to Hg salts, and waste samples collected from within the acid pit. The instrumentation used included a quadrupole-based SIMS instrument and an ion trap SIMS instrument.

RESULTS

Analysis of Hg Salts

Initial attempts to characterize Hg species using quadrupole-based SIMS instrument resulted in the facile identification of mercuric chloride and sulfate salts, which produce stable HgCl_3^- and HgSO_4^- adduct ions under the low pressure conditions of the quadrupole (Figure 1). The ion signature of mercuric chloride and sulfate salts comprises these two ions. In contrast, however, the important nitrate and oxide species, $\text{Hg}(\text{NO}_3)_2$ and HgO , produced no signature when analyzed using the quadrupole.

<u>Hg species</u>		<u>Ions observed using SIMS</u>
HgCl ₂	$\xrightarrow{\text{SIMS}}$	HgCl ₃
HgSO ₄	$\xrightarrow{\text{SIMS}}$	HgSO ₄
Hg(NO ₃) ₂	$\xrightarrow{\text{SIMS}}$	no signature
HgO	$\xrightarrow{\text{SIMS}}$	no signature

Figure 1. Characteristic ions observed in the SIMS spectra of Hg salts, acquired using the quadrupole instrument.

Because both the nitrate and oxide species are important candidates in the acid pit waste, the study of the Hg salts was pursued using a new generation instrument based on an ion trap mass analyzer. The principle difference between the ion trap and the quadrupole is that the ion trap operates using a bath gas, which stabilizes otherwise fragile Hg-signature ions, and thus permits their observation. When Hg(NO₃)₂ was analyzed using the ion trap SIMS, no Hg-nitrate ions could be observed, but abundant ions that corresponded to Hg(C₆H₁₁NH)₂H⁺ were formed (Figure 2). The origin of these ions was the reaction of atmospheric cyclohexylamine (C₆H₁₁NH₂) with Hg(NO₃)₂. When this reaction was attempted starting with HgCl₂ and other Hg salts, the Hg amine complex ion could not be observed. Hence, this reaction is a signature for the presence of mercuric nitrated on mineral surfaces.

<u>Hg species</u>		<u>Ions observed using SIMS</u>
Hg(NO ₃) ₂	$\xrightarrow[\text{SIMS}]{\text{C}_6\text{H}_{11}\text{NH}_2}$	Hg(C ₆ H ₁₁ NH) ₂ H ⁺
HgCl ₂	$\xrightarrow[\text{SIMS}]{\text{C}_6\text{H}_{11}\text{NH}_2}$	no signature
HgO	$\xrightarrow[\text{SIMS}]{\text{C}_6\text{H}_{11}\text{NH}_2}$	no signature

Figure 2. Formation of Hg-amine complexes, observable using the ion trap SIMS instrument.

HgO would not react with cyclohexylamine, but would react with formic acid (HCO_2H) vapor to produce an ion that corresponded to HgHCO_2^- . None of the other Hg salts would produce this ion, and hence this reaction constituted a signature for HgO.

Red Clay Doped with Hg Salts

The above series of analyses and surface derivatization reactions constitute a reasonable starting point for an investigation of Hg in contact with minerals common to the acid pit waste. A red clay sample was chosen for investigation because it forms a significant layer in the subsurface of the acid pit area. The sample was collected from the surface near the RWMC. At the collection point, the interbed, which contains the red clay, comes to the surface, although at the RWMC this layer is 20 to 40 feet below the surface.

The red clay was doped with Hg chloride, nitrate, and oxide in concentrations ranging from approximately 100 ppm to about 1%. Subsamples were then treated with vapor-phase $\text{C}_6\text{H}_{11}\text{NH}_2$, and HCO_2H . When the treated samples were analyzed, no signal was observed that corresponded to $\text{Hg}(\text{C}_6\text{H}_{11}\text{NH}_2)_2\text{H}^+$ or HgHCO_2^- . Thus it is unlikely that substantial concentrations of Hg nitrate or oxide are present on the red clay. For these systems, it is hypothesized that the Hg is complexed to anionic aluminate or silicate sites on the mineral surface (Figure 3), and that the Hg-mineral complexes are strong enough so that neither $\text{C}_6\text{H}_{11}\text{NH}_2$ nor HCO_2H is a strong enough ligand to displace the surface bonding. This remains a hypothesis because a direct analysis specific for Hg-aluminate or Hg-silicate has not been developed yet.

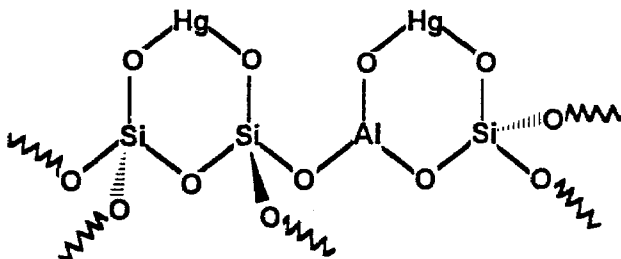


Figure 3. Hypothetical structure for Hg complexed with anionic sites on the aluminosilicate matrix of red clay.

When the red clay that was doped with HgCl_2 was examined, Hg-bearing ions could be observed. This indicates that the basic moieties on the aluminosilicate matrix may be incapable of displacing the Cl^- ligand on Hg.

Analysis of Acid Pit Samples

A variety of samples were collected from within the acid pit and submitted for analysis, including a white mineral, which was predominantly lime, soil, and debris. The samples were screened as received, and subsequent to treatment with $C_6H_{11}NH_2$ and HCO_2H . In none of the analyses were Hg-bearing ions observed.

This result indicates that no substantial concentrations of Hg nitrate, formate, or chloride are present on the surface of these samples. The presence of substantial lime in these samples suggests that another possibility is $HgCO_3$, but a test for the presence of this species has not been developed.

CONCLUSIONS

The results of secondary ion mass spectrometry analyses indicate the absence of substantial nitrate and chloride species on the surfaces of red clay and carbonate, both of which are typical in the acid pit, and the debris samples from the acid pit. This results constitute negative analyses for the actual species of Hg present. On the basis of the fact that $Hg(NO_3)$ cannot be observed, it is felt that complexation by silicate and aluminate moieties on the soil surface is responsible for strong retention of Hg, which is consistent with the earlier conclusion that the metal does not appear to be moving.

REFERENCES

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